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6/24/01
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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE



Application of: N. EL KHIATI *et al.*

Application No.: 09/242,803

Group Art Unit: 1755

Filed: February 24, 1999

Examiner: D. Sample

For: SODA-LIME-SILICA GLASS
COMPOSITIONS AND APPLICATIONS

Attorney Docket No.: 3633-461

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JUN 22 2001

TC 1700

SUBMISSION OF CERTIFIED TRANSLATIONS OF PRIORITY DOCUMENTS

Assistant Commissioner for Patents
Washington, D.C. 20231

Sir:

Applicant has claimed priority under 35 U.S.C. § 119 to German Application No. 197 10 289.1, filed March 13, 1997, French Application No. 97/05364, filed April 30, 1997, and French Application No. 97/07521, filed June 17, 1997. In support of these claims, certified copies of said applications are submitted herewith.

No fee is believed to be due for this submission. Should any fees be required, however, please charge such fees to Pennie & Edmonds LLP Deposit Account No. 16-1150.

Respectfully submitted,

Paul E. [Signature] (45,627)

Date June 15, 2001

for Marcia H Sundeen 30,893
Marcia H. Sundeen (Reg. No.)

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I, Elisabeth Ann LUCAS,

Director of RWS Group plc, of Europa House, Marsham Way, Gerrards Cross, Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That the translator responsible for the attached translation is well acquainted with the German and English languages.
3. That the attached is, to the best of RWS Group plc knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in Germany on March 13, 1997 under the number 197 10 289.1 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

A handwritten signature in black ink, appearing to read "Elisabeth Ann".

For and on behalf of RWS Group plc

The 20th day of April 2001



FEDERAL REPUBLIC OF GERMANY

CERTIFICATE

VETROTECH SAINT-GOBAIN (INTERNATIONAL) AG

of

Walchwil/Switzerland

have filed a Patent Application under the title:

"Fire-resistant glazing"

on 13 March 1997 at the German Patent Office.

The attached document is a correct and accurate reproduction of the original submission for this Patent Application.

The German Patent Office has for the time being given the Application the symbols C 03 V and C 03 B of the International Patent Classification.

Munich, 23 February 1998
President of the German Patent Office

pp

Schulenburg

File No: 197 10 289.1



Abstract

Fire-resistant glazing of fire-resistance classes G is produced from glass panes having safety-glass properties which have been tempered in a conventional tempering unit using glasses which have a coefficient of thermal expansion α_{20-300} of from 6 to $8.5 \cdot 10^{-6} K^{-1}$, a thermal stress factor φ of from 0.5 to 0.8 N/(mm²·K), a softening point of from 750 to 830°C and a maximum working point of 1190°C.

Fire-resistant glazing

Description

5 The invention relates to fire-resistant glazing of fire-resistance classes G comprising a silicate glass pane having safety-glass properties which has been tempered in a conventional tempering unit with air quenching.

10 Fire-resistant glazing of fire-resistance classes G must, including its frame and holder, prevent the passage of fire and smoke for a certain time in a DIN 4102 or ISO/DIS 834-1 fire test. During this time, the glass panes must neither crack under the effect of
15 the stresses formed by the temperature gradients between the pane area and the clamped edge, nor exceed their softening point during this time, since otherwise they lose their strength and thus open the opening. They are classified in fire-resistance class G 30,
20 G 60, G 90 or G 120 corresponding to the time in minutes for which they withstand the fire.

25 Fire-resistant glass panes are usually held in frames which screen the edge of the glass panes against the action of heat to a certain extent. The resultant temperature gradient between the pane centre and the edge results in considerable tensile stresses in the edge region and in destruction of the glass panes if special measures are not taken to compensate for these tensile stresses. These measures consist in tempering
30 the glass panes, which produces strong compressive stresses in the edge region. The tempering also allows safety-glass properties to be imparted on the glass pane if the tempering is carried out in such a way that the glass pane breaks into small granules when it is
35 fractured.

The level of the stresses in the pane area and in the edge region can in principle be measured by optical methods. However, optical measurement is relatively complex. In practice, therefore, there has
5 been a trend toward determining the stress state via the flexural tensile strength achieved by the tempering, in accordance with DIN 52303 or EN 12150. It has been found empirically here that it is necessary to produce a flexural tensile strength of at least
10 120 N/mm² if the glass pane is to withstand the tensile stresses produced by the temperature gradient at the edge. Since untempered glass panes have a basic flexural tensile strength of about 50 N/mm², this means that it is necessary to increase the flexural tensile
15 strength by at least 70 N/mm² by the tempering. The numerical value of this increase in the flexural tensile strength corresponds directly to the level of surface compressive stresses.

A further increase in the fire resistance time
20 can be achieved by increasing the border depth of the glass pane in the frame. For a flexural tensile strength of the glass pane of 120 N/mm² and a border depth of 10 mm, the glazing conforms, for example, to fire resistance class G 30, while a border depth of
25 20 mm allows fire resistance class G 90 to be achieved.

Glass panes made from conventional float glass (soda-lime silicate glass) can be tempered well using conventional tempering units since these glass compositions have a relatively large coefficient of
30 thermal expansion of greater than $8.5 \cdot 10^{-6} \text{K}^{-1}$. Conventional float glass allows flexural tensile strengths of up to 200 N/mm² to be achieved. Under the action of the tensile stresses produced by the temperature gradient, they therefore do not crack for a
35 glass border of about 10 mm, but lose their strength owing to their relatively low softening point of about 730°C. Tempered glass panes made from float glass therefore at best satisfy fire-resistance class G 30 under normal installation conditions.

However, monolithic glass panes having fire-resistance class G 60 or above are also known. These consist of glass compositions having a high softening point of above 815°C and consequently have a long time-to-failure in the fire test. Heat-resistant borosilicate and aluminosilicate glasses are particularly suitable for this purpose. However, these glass panes too must be tempered if they are to withstand the high tensile stresses produced in the edge region in the fire test.

The use of tempering for fire-protection glasses made from heat-resistant borosilicate or aluminosilicate glasses is disclosed in DE 2313442 B2 and DE 2413552 B2. According to these publications, the only glasses suitable for tempering are those whose product of thermal expansion α and modulus of elasticity E is from 1 to 5 $\text{kp}\cdot\text{cm}^{-2}\cdot\text{°C}^{-1}$, i.e. borosilicate or aluminosilicate glasses having a thermal expansion of $\alpha_{20-300} = 3$ to $6.5 \cdot 10^{-6} \text{ °C}^{-1}$. However, the requisite edge tempering of these glass panes cannot be achieved with the aid of conventional air tempering units, but is achieved by a special process in which the glass panes are placed, during heating, between somewhat smaller ceramic plates, so that the edge of the glass pane projects beyond the ceramic plates and is therefore cooled faster, while the pane centre is cooled more slowly under the action of the ceramic plates. Although the requisite edge tempering can be produced in this way, the glass panes produced in this way do not have safety-glass properties.

DE 4325656 C2 discloses producing monolithic fire-protection glasses using glasses which have a coefficient of thermal expansion α of between 3 and $6 \cdot 10^{-6} \text{ K}^{-1}$, a specific thermal stress ϕ of between 0.3 and 0.5 $\text{N}/(\text{mm}^2 \cdot \text{K})$, a softening point (= temperature at viscosity $10^{7.6} \text{ dPas}$) of above 830°C and a working point (= temperature at viscosity 10^4 dPas) of from 1190° to 1260°C. The specific thermal stress is the glass-specific parameter calculated from the coefficient of

thermal expansion α , the modulus of elasticity E and the Poisson constant μ according to the formula $\varphi = \alpha \cdot E / (1 - \mu)$. Glasses having these physical properties can be provided in a conventional air tempering unit
5 both with the requisite compressive stress of the edge and with the stress necessary to produce fine granules over the entire area, so that no special tempering measures are necessary and the production process is thus significantly simplified. However, glasses having
10 these physical properties necessarily contain B_2O_3 , Al_2O_3 and ZrO_2 in amounts which hinder the melting process and the processing. They cannot be produced by the float process, which has proven successful owing to its economy, since their working point is too high and in
15 addition the melting process requires particular measures.

Although DE 2818804 B2 discloses borosilicate glass compositions which are intended for use as fire-protection glasses and which, owing to a relatively low
20 working point, can be processed by the float glass process and can also be tempered in conventional tempering units, these glasses contain, however, from 11.5 to 14.5% of B_2O_3 and in addition have similar physical properties to the glasses disclosed in
25 DE 4325656 C2. The compressive stresses achievable by air quenching and the flexural tensile strength of these glasses are also restricted to relatively low values, and in addition these glasses have the problems and disadvantages known in the processing of boro-
30 silicate glasses.

The invention has the object of providing monolithic fire-protection glasses of fire-resistance classes G which on the one hand can be tempered in conventional air tempering units, but on the other hand
35 comprise glass compositions which can be processed economically and with no technical problems and can be converted by the conventional float glass process into flat glass which has a comparable aspect and optical properties to known float glass.

This object is achieved according to the invention by using glasses which have a coefficient of thermal expansion α_{20-300} of from 6 to $8.5 \cdot 10^{-6} \text{ K}^{-1}$, a thermal stress factor ϕ of from 0.5 to 0.8 N/(mm²·K), a softening point (viscosity = $10^{7.6}$ dPas) of from 750° to 830°C and a maximum working point (viscosity = 10⁴ dPas) of 1190°C.

Glass compositions which have these physical properties can be selected from known glass compositions, although it must be ensured that these glass compositions contain no or at least very little B₂O₃ and Al₂O₃.

It has been found that glasses having the properties according to the invention can not only be processed relatively well, but that they are particularly suitable for the production of monolithic fire-protection glasses since they have significantly higher flexural tensile strength, even in the case of conventional air tempering, than the borosilicate and aluminosilicate glasses known for the production of fire-protection glasses. This is because, owing to their greater coefficient of thermal expansion and their greater thermal stress factor, significantly greater flexural tensile strengths, i.e. significantly greater compressive stresses, can be produced in conventional tempering units, so that the achievable temperature difference strength (TDS) between the clamped cold edge and the hot pane centre is significantly greater. On the other hand, it has been found that the time-to-failure of these glasses is entirely sufficient to satisfy fire-resistance class G 30, even with a pane thickness of only 5 mm and a border depth in the frame of 10 mm. However, the glasses used in accordance with the invention also allow the higher fire-resistance classes G 60 and G 90 and even G 120 to be achieved if, where appropriate, glass panes of greater thickness and frames having a wider glass border are used, i.e. frames which cover the edge of

the glass pane to a greater extent, for example up to 25 mm.

Further advantages and expedient embodiments and refinements of the invention are indicated in the 5 subclaims and the following description of various working examples.

Example 1

The fire-protection glass is produced using a flat-glass pane with a thickness of 5 mm produced by 10 the float process and having the following composition, in % by weight: 75.4% of SiO₂, 11.0% of Na₂O, 12.0% of CaO, 1.0% of Al₂O₃, 0.3% of K₂O, 0.3% of other oxides.

This glass has the following physical properties:

15	Coefficient of thermal expansion	α_{20-300}	= $7.6 \cdot 10^{-6} \text{K}^{-1}$
	Thermal stress factor	ϕ	= 0.69 N/(mm ² ·K)
	Modulus of elasticity	E	= $7.14 \cdot 10^4 \text{ N/mm}^2$
	Poisson constant	μ	= 0.215
	Softening point	SP	= 761°C
20	Working point	WP	= 1061°C

A number of glass panes measuring 90 × 55 cm² were finely ground on the edges and tempered horizontally in a conventional air tempering unit. To this end, they were warmed to a temperature of about 670°C and 25 cooled quickly using two conventional blow boxes. The blow boxes were provided with jets arranged 3 cm apart in rows about 8 cm from one another. The diameter of the jet opening was 8 mm. The distance of the jet openings from the glass surface was about 5 cm, and the 30 static pressure of the air in the blow boxes was 7.5 kPas ± 10%.

Measurements of the flexural tensile strength of the tempered glass panes by the process described in EN 12150 gave flexural tensile strengths of the glass 35 panes of 210 ± 10 N/mm². This value corresponds to a surface compressive stress of about 160 N/mm².

Fire tests in accordance with the ISO/DIS 834-1 standard were carried out on three glass panes of this type, with the glass border in the frame being 10 mm.

The glass panes withstood the fire for 65 min in two fire tests and for 71 min in the third fire test. This fire-protection glazing thus satisfies the conditions of fire-resistance class G 60.

5 Example 2

The glass panes used had a thickness of 6 mm and the composition indicated in Example 1 and were likewise produced by the float glass process. The glass consequently had the same physical properties as in 10 Example 1. In this case, a number of glass panes measuring $70 \times 150 \text{ cm}^2$ were finely ground at the edge and tempered under the same conditions as in Example 1.

Measurements of the flexural tensile strength of these tempered glass panes gave values of 15 $250 \pm 15 \text{ N/mm}^2$. Fire tests were carried out on three of these glass panes with a thickness of 6 mm, with the glass border in the metal frame in these experiments being 15 mm. In all three fire tests, the time-to-failure was greater than 90 min, so that these fire-20 protection glasses having a thickness of 6 mm and a border depth of 15 mm in the frame satisfy the conditions of fire-resistance class G 90.

Example 3

The fire-protection glass was produced using a 25 glass having the following composition: 67.0% of SiO_2 , 10.0% of CaO , 2.0% of MgO , 2.5% of SrO , 7.0% of Na_2O , 5.0% of K_2O , 1.0% of Al_2O_3 , 5.5% of ZrO_2 .

This glass has the following physical properties:

30	Coefficient of thermal expansion α_{20-300}	$= 7.9 \cdot 10^{-6} \text{ K}^{-1}$
	Thermal stress factor	$\phi = 0.76 \text{ N}/(\text{mm}^2 \cdot \text{K})$
	Modulus of elasticity	$E = 7.7 \cdot 10^4 \text{ N/mm}^2$
	Poisson constant	$\mu = 0.21$
	Softening point	$SP = 800^\circ\text{C}$
35	Working point	$WP = 1190^\circ\text{C}$

The molten glass is used to produce a glass band with a thickness of 8 mm by the float process. A number of glass panes measuring $150 \times 70 \text{ cm}^2$ were finely

ground at the edges and tempered as described in Example 1 in a conventional air tempering unit.

Measurements of the flexural tensile strength of the tempered glass panes gave values of
5 $235 \pm 10 \text{ N/mm}^2$.

Fire tests in accordance with the above standard were carried out on three such tempered glass panes having a thickness of 8 mm, in this case with a glass border of 22 mm in a steel frame. In all three
10 fire tests, the time-to-failure was longer than 120 min, so that this fire-protection glazing satisfies the conditions of fire-resistance class G 120.

Patent Claims

1. Fire-resistant glazing of fire-resistance classes G, comprising a silicate glass pane having safety-glass properties which has been tempered in a conventional tempering unit with air quenching, characterized by the use of glasses having a coefficient of thermal expansion α_{20-300} of from 6 to $8.5 \cdot 10^{-6} K^{-1}$, a thermal stress factor ϕ of from 0.5 to 0.8 N/(mm²·K), a softening point (viscosity = $10^{7.6}$ dPas) of from 750° to 830°C and a maximum working point (viscosity = 10⁴ dPas) of 1190°C.

2. Fire-resistant glazing according to Claim 1, characterized in that the glasses used have a coefficient of thermal expansion α_{20-300} of from 6.5 to $7.5 \cdot 10^{-6} K^{-1}$, a thermal stress factor ϕ of from 0.6 to 0.7 N/(mm²·K) and a softening point of from 800° to 820°C.

3. Fire-resistant glazing according to Claim 1, characterized by the following glass composition, in % by weight:

SiO ₂	73 - 76
CaO	11 - 13
Na ₂ O	10 - 12
K ₂ O	0.1 - 0.5
Al ₂ O ₃	0.5 - 1.5

4. Fire-resistant glazing according to Claim 1, characterized by the following glass composition, in % by weight:

SiO ₂	65 - 69
CaO	9 - 11
MgO	1 - 3
SrO	2 - 4
Na ₂ O	6 - 8
K ₂ O	4 - 6
Al ₂ O ₃	0.5 - 1.5
ZrO	4 - 6

25 5. Fire-resistant glazing according to one of Claims 1 to 4, characterized in that the glass pane has

- 11 -

a surface compressive stress of from 120 to 200 N/mm²,
preferably of from 150 to 190 N/mm².

UNITED STATES PATENT AND TRADEMARK OFFICE

I, Roger Walter GRAY MA, DPhil, CPhys,
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,
Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the French and English languages.
3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in France on June 17, 1997 under the number 97/07,521 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.



For and on behalf of RWS Group plc

The 20th day of April 2001

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The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, 10 MARCH 1998

On behalf of the Director-General of the
Institut National de la Propriété Industrielle
The Patent Department Head

(signature)

Martine PLANCHÉ

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DATE OF SUBMISSION OF THE DOCUMENTS 17 JUNE 1997
NATIONAL REGISTRATION 97/07,521
DEPARTMENT OF FILING 75
DATE OF FILING 17 JUNE 1997

1. NAME AND ADDRESS OF THE APPLICANT OR THE REPRESENTATIVE TO WHOM THE CORRESPONDENCE IS TO BE ADDRESSED

Mr Stéphane LE CAM

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2. APPLICATION Nature of the industrial property right
 patent divisional application
→ initial application
 utility certificate conversion of a European patent application patent

No. of permanent power of attorney

422-5/S-006

Correspondent's references

SL2 1997044 FR

Telephone

01 48 39 59 58

utility certificate No.

date

Compilation of the search report

deferred immediate

The applicant, as a physical person, asks to pay the fee by instalments

yes no

Title of the invention (maximum 200 characters)

SILICA-SODA-LIME GLASS COMPOSITION [sic] AND THEIR APPLICATIONS

3. APPLICANT(S) SIREN No. APE-NAF code

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If insufficient space, continue on plain paper

4. INVENTOR(S) The inventors are the applicants yes no If the answer is no, provide a separate designation

5. REDUCTION OF THE RATE OF FEES requested for the first time requested prior to filing; attach copy of the favourable decision

6. PRIORITY DECLARATION OR APPLICATION FOR THE BENEFIT OF THE FILING DATE OF A PRIOR APPLICATION

Country of origin

Number

Filing date

Nature of the application

7. DIVISIONS previous to the present application

No.

date

No.

date

1. SIGNATURE OF THE APPLICANT OR REPRESENTATIVE
(name and capacity of the signatory - registration No.)

SIGNATURE OF THE RECEIVING OFFICIAL

SIGNATURE AFTER REGISTRATION OF THE APPLICATION AT THE INPI

[Rubber stamp of

SAINT-GOBAIN RECHERCHE]

(illegible signature)

(signature)

Stéphane LE CAM

SILICA-SODA-LIME GLASS COMPOSITION [sic] AND THEIR APPLICATIONS

The invention relates to silica-soda-lime glass
5 compositions suitable for being converted into a ribbon
of glass from which may be cut sheets which, in
particular after treatment, exhibit heat resistance.

Such sheets may more particularly be used for
producing fireproof glazing panels or for serving as
10 substrates for the manufacture of plasma screens,
electroluminescent screens and cold-cathode screens
(field-emission display).

The invention will be described more
particularly with reference to a glazing panel which is
15 fire resistant according to the G fire resistance
classes. Such a glazing panel consists of a thermally
toughened sheet of glass and has properties of a safety
glass.

Glazing panels fire resistant in accordance
20 with the G fire resistance classes, together with their
frames and their fittings, must offer resistance, in a
fire withstand test according to the standard DIN 4102
or to the standard ISO/DIS 834-1, for a certain time,
to the passage of the fire and smoke. During this time,
25 the glazing panels must neither break, under the effect
of the stresses which occur as a result of the
temperature gradients between the surface of the
glazing panel in contact with the heat and the embedded
edge, nor exceed their softening point, since they
30 would lose their stability and would thus expose the
opening. They are ranked in the fire resistance classes
G 30, G 60, G 90 or G 120 depending on the time in
minutes for which they withstand fire.

In general, fire-resistant glazing panels are
35 held in frames which protect, to a greater or lesser
extent, the edge of the said glazing panels from the
effect of the heat. The temperature gradient which thus
occurs between the middle of the glazing panel and the
edge generates considerable tensile stresses in the

marginal region and results in the destruction of the glazing panels if special measures are not taken to compensate for these tensile stresses. These measures consist of thermally toughening the glazing panels,
5 this toughening making it possible to induce large initial compressive stresses in the marginal region. The thermal toughening gives the glazing panel additional properties of a safety glass when the toughening is carried out in such a way that, should
10 the glazing panel break, it would do so by fragmenting into tiny pieces.

The initial stress state is usually determined by means of the flexural/tensile strength obtained by the toughening operation, in accordance with the
15 standard DIN 52303 or to the standard EN 12150. Experiments have in this case shown the need to guarantee a flexural/tensile strength of at least 120 N/mm² so that the glazing panel can withstand the tensile stresses generated by the temperature gradients
20 at the edge. Given that untoughened glazing panels have a basic flexural/tensile strength of approximately 50 N/mm², this means that it is necessary to increase this strength, by toughening, by at least 70 N/mm². The value of this increase in the flexural/tensile strength
25 corresponds directly to the value of the initial compressive surface stresses.

It is also possible to increase the fire resistance time by increasing the depth of insertion of the glazing panel in the frame. In the case of a
30 flexural/tensile strength of the glazing panel of 120 N/mm² and an insertion depth of 10 mm, the glazing panel conforms, for example, to the fire resistance class G 30, while an insertion depth of 20 mm allows it to achieve the fire resistance class G 90.

35 Glazing panels made of the usual float glass (soda-lime-based silica glass) may be suitably toughened by means of conventional toughening plants, given that these glass compositions have relatively high thermal expansion coefficients, greater than 85 ×

10^{-7} K $^{-1}$. The usual float glass allows flexural/tensile strengths possibly ranging up to 200 N/mm 2 to be achieved. Under the effect of the tensile stresses generated by the temperature gradients, the glazing 5 panels consequently do not break if the insertion depth is approximately 10 mm, but they lose their stability because of their relatively low softening temperature of approximately 730°C. Toughened glazing panels made of float glass therefore conform, under standard 10 installation conditions, at the very most to the fire resistance class G 30.

However, monolithic glazing panels of fire resistance class G 60 and higher classes are also known. These glazing panels consist of glass 15 compositions having a high softening point of greater than 815°C and consequently have a long resistance time in a fire withstand test. In this case, borosilicate- and aluminosilicate-based heat-resistant glasses prove to be particularly suitable. However, these types of 20 glass must also be toughened thermally in order to be able to withstand the high tensile stresses which occur in the marginal region in a fire withstand test.

The use of thermal toughening for fireproof glazing panels whose glass compositions are based on 25 heat-resistant borosilicate or on heat-resistant aluminosilicate is known from the documents DE 2,313,442 B2 and US 3,984,252. According to these documents, only suitable for toughening are glasses for which the product of the thermal expansion α and the 30 modulus of elasticity E reaches 1 to 5 kp.cm $^{-2} \cdot ^\circ\text{C}^{-1}$, i.e. borosilicate- or aluminosilicate-based glasses having a thermal expansion of $\alpha_{20-300} = 30$ to $65 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$. However, the necessary toughening at the edge of these 35 glazing panels cannot be carried out by means of conventional air-toughening plants but requires a special process in which the glazing panels are placed, during the heating, between slightly smaller ceramic tiles in such a way that the edge of the glazing panel extends beyond the ceramic tiles and is therefore

cooled more rapidly, while the middle of the glazing panel cools more slowly due to the effect of the ceramic tiles. The necessary toughening at the edge may, to be sure, be achieved in this way, but the
5 glazing panels thus manufactured do not have any safety-glass properties.

It is known from the document EP-A-638,526 to use, for the manufacture of monolithic fireproof glazing panels, glass compositions which have a thermal
10 expansion coefficient α of between 30 and $60 \times 10^{-7} \text{ K}^{-1}$, a φ coefficient of between 0.3 and 0.5 N/(mm².K), a softening point (= temperature for a viscosity of 10^{7.6} poise) of greater than 830°C and a working point
15 (= temperature for a viscosity of 10⁴ poise) of between 1190° and 1260°C. The φ coefficient or specific thermal stress is the specific parameter of the glass calculated from the thermal expansion coefficient α , the modulus of elasticity E and Poisson's ratio μ according to the formula $\varphi = \alpha \cdot E / (1 - \mu)$. Glazing panels
20 having these physical properties may acquire, in a conventional air-toughening plant, both the initial compressive stresses necessary at the edge and the toughening stresses exerted over the entire surface and necessary for obtaining fragmentation into tiny pieces,
25 so that no particular measurement is necessary in respect of the toughening operation and so that the manufacturing process is thereby considerably simplified. However, glazing panels having these physical properties necessarily contain B₂O₃, Al₂O₃ and
30 ZrO₂ in quantities which complicate the melting process and the conversion process. These glazing panels thus cannot be manufactured using the floating process which has proved to be exceptionally economical, given that their conversion point is too high and that the melting
35 furthermore requires special measures.

Borosilicate-based glass compositions are known, from the document FR-2,389,582, which are provided, to be sure, for use in fireproof glazing panels which, because of their relatively low

conversion point, may melt during the floating process and also be toughened by means of conventional toughening plants. However, these glasses contain from 11.5 to 14.5% of B_2O_3 , and also have physical properties 5 similar to those of the glasses known from the document EP-A-638,526. Even in the case of these glasses, the initial compressive stresses and the flexural or the tensile strength which may be achieved by air toughening are limited to relatively low values and 10 these glasses also have the known difficulties and drawbacks when melting borosilicate-based glasses.

The subject of the invention is thus novel glass compositions for the manufacture of glazing panels which are fire resistant according to the G fire 15 resistance classes which, on the one hand, may be thermally toughened by means of conventional plants and which, on the other hand, can be melted without any economic and/or technological problems and which can be converted into flat glass using the float process.

20 This object is achieved according to the invention by a glass composition of the silica-soda-lime type, intended for the manufacture of substrates or sheets, the said glass composition having a ϕ coefficient of between 0.5 and 0.85 $N/(mm^2 \cdot ^\circ C)$, a 25 working point (viscosity = 10^4 poise) of less than $1200^\circ C$ and satisfying the relationship:

$$\phi^2 \cdot c/a < 2 \text{ MPa}^2/\text{ }^\circ \text{C}^2.$$

As mentioned previously, the ϕ coefficient is defined according to the relationship:

30
$$\phi = \alpha \cdot E / (1 - \mu)$$

where α : expansion coefficient

E : modulus of elasticity

μ : Poisson's ratio.

The modulus of elasticity and Poisson's ratio 35 are determined by the following test: a glass test piece having the dimensions $100 \times 10 \text{ mm}^2$ and a thickness of less than 6 mm is subjected to 4-point bending in which the outer bearing points are separated by 90 mm and the inner bearing points 30 mm. A strain gauge is

bonded to the centre of the glass plate. The main strains (in the length of the plate and in its width) are deduced therefrom. The stress applied is calculated from the force applied. The equations between the
5 principal stress and strains allow the modulus of elasticity and Poisson's ratio to be determined.

The "c/a" value is defined by the brittleness test described below: the glass is firstly annealed so as to remove the residual stresses. The glass is heated
10 at its annealing point for 1 hour and then cooled at 2°C/min to ambient temperature. The glass test piece to be tested is indented with a 200 g load for 30 seconds at ambient temperature. The diagonals of the Vickers impression and the size of the radial cracks (Lawn and
15 Marshall, J. Am. Cer. Soc. 62, 347-350 (1979); Sehgal et al., J. Mat. Sci. Let. 14, 167-169 (1995)) are measured 72 hours after indentation. The c/a ratio, i.e. length of the radial cracks/semi-diagonal, is measured on 10 indentations so as to obtain sufficient
20 statistics.

Preferably, the glass composition according to the invention satisfies [lacuna]:

$$\phi^2 \cdot c/a > 0.70 \text{ MPa}^2/\text{°C}^2.$$

Also preferably, the product $\phi^2 \cdot c/a$ is greater
25 than 1 and preferably less than 1.8.

In one embodiment of the invention and more particularly in the case of the production of substrates for plasma screens, the composition has a strain point of greater than 570°C and preferably
30 greater than 600°C. More particularly also for applications of the plasma-screen type, the ϕ coefficient is between 0.75 and 0.85 and preferably less than 0.8.

For fireproof glazing panel applications, the ϕ
35 coefficient is advantageously less than 0.8 and preferably greater than 0.7.

According to a preferred variant of the invention, the glass compositions according to the invention have a softening point (viscosity = $10^{7.6}$

poise) of greater than 750°C. Also preferably, the working point of the glass compositions according to the invention is less than 1190°C.

The inventors have been able to demonstrate
5 that glasses having the properties in accordance with
the invention may not only melt relatively well but, in
addition, are particularly suitable for the manufacture
of monolithic fireproof glazing panels insofar as, even
in the case of conventional air toughening, they have a
10 flexural/tensile strength markedly greater than that of
the known borosilicate- and aluminosilicate-based
glasses for the manufacture of fireproof glazing
panels. By virtue of their higher thermal expansion
coefficient and their higher α coefficient, it is
15 possible in fact to obtain, by means of standard
toughening plants, flexural/tensile strengths markedly
greater, i.e. markedly greater initial compressive
stresses, so as to increase substantially the
resistance to the temperature difference which may
20 exist between the embedded cold edge and the hot centre
of the glazing panel. Furthermore, it was apparent that
the resistance of these glasses was entirely sufficient
for meeting the fire resistance class G 30 even in the
case of a depth of insertion in the frame of 10 mm.
25 However, the glasses used in accordance with the
invention also make it possible to achieve superior
fire resistance classes of G 60, G 90 or even G 120
when, as required, thicker glazing panels are used and
a frame is used in which they are embedded more deeply,
30 i.e. a frame which covers the edge of the glazing panel
to a greater extent, for example up to 25 mm.

According to a preferred embodiment of the
invention, the glass composition contains the
constituents below in the following proportions by
35 weight:

SiO ₂	55 - 75%
Al ₂ O ₃	0 - 7%
ZrO ₂	0 - 8%
Na ₂ O	5 - 10%

K ₂ O	0 - 8%
CaO	8 - 12%.

The glass compositions according to the invention have, in particular, the advantage of being
5 able to be melted and converted into glass ribbon form at temperatures close to those adopted for the manufacture of conventional silica-soda-lime glass.

In this regard, SiO₂ plays an essential role. In the context of the invention, the SiO₂ content must not
10 exceed approximately 75%; above this, the melting of the batch and the refining of the glass require high temperatures which cause accelerated wear of the furnace refractories. Below 55% by weight of SiO₂, the glasses according to the invention are insufficiently
15 stable.

Alumina acts as a stabilizer. This oxide to some extent increases the chemical resistance of the glass and increases the strain-point temperature. The percentage of Al₂O₃ preferably does not exceed 5% and
20 preferably 3%, in particular so as not to increase unacceptably the viscosity of the glass at high temperatures.

ZrO₂ also acts as a stabilizer. This oxide to a certain extent increases the chemical resistance of the
25 glass and increases the strain-point temperature. ZrO₂ is advantageously present with a content higher than 1% and must not exceed 8% for fear of making the melting operation too difficult. Although this oxide is difficult to melt, it has the advantage of not
30 increasing the viscosity of the glasses according to the invention at high temperatures, in the same way as SiO₂ and Al₂O₃. The oxide B₂O₃ may also be present with a content of at most 3%, and preferably less than 2%. This oxide also makes it possible to increase the
35 fluidity of the glass without lowering the strain point.

Overall, the melting of the glasses according to the invention remains within acceptable temperature limits, as long as the sum of the SiO₂, Al₂O₃ and ZrO₂

oxide contents remains less than or equal to 75%. The expression "acceptable limits" should be understood to mean that the temperature of the glass corresponding to log η_2 , [sic] does not exceed approximately 1550°C and 5 preferably 1510°C.

Moreover, it seems that these glasses lead to little corrosion of the refractories of the AZS (alumina-zirconia-silica) type normally used in this type of furnace. These glasses thus guarantee that the 10 operating time of the furnace is optimized.

Moreover, there is a sufficient difference in the glass compositions according to the invention between the glass-forming temperature and its liquidus temperature; this is because, in the float-glass 15 technique in particular, it is important that the liquidus temperature of the glass remain equal to or less than the temperature corresponding to log $\eta = 3.5$, which is the case with the glasses according to the invention. This difference is advantageously at least 20 10°C to 30°C. These differences or working ranges, which might seem "narrow" for standard silica-soda-lime glasses intended for manufacturing glazing panels, are sufficient here to ensure high-quality forming without adopting excessively extreme conditions for operating 25 the furnace. This is because the glasses are quite special, for applications of the high-tech, high value-added type, such as plasma screens, in which one may "indulge" in very precise control and suitability of the operation of the furnace: "accessible" working 30 ranges are maintained without upsetting the furnace or exposing it to risk.

The influence of the other oxides on the ability of the glasses according to the invention to be melted and floated on a metal bath, as well as their 35 properties, is as follows: the oxides Na₂O and K₂O make it possible to maintain the melting temperature of the glasses according to the invention and their high-temperature viscosities within the limits indicated above. To do this, the sum of the contents of these

oxides remains greater than 8% and preferably greater than 10%.

Provision may also be made to incorporate lithium oxide Li_2O in the glass composition according to 5 the invention, especially as a fluxing agent, with contents of possibly as much as 3% and preferably not exceeding 1%.

The alkaline-earth metal oxides introduced into the glasses according to the invention have the overall 10 effect of raising the strain-point temperature, and it is for this reason that the sum of their weight contents must be at least equal to 12%. Above approximately 20%, the ability of the glasses to devitrify may increase to an extent incompatible with 15 the process of floating on a metal bath. In order to keep the devitrification of the glasses within acceptable limits, their CaO and MgO weight contents must not exceed 11% and 5% respectively. The MgO content is preferably equal to or less than 2%.

20 MgO , CaO and, to a lesser degree, SrO make it possible to increase the strain-point temperature; BaO and SrO make it possible to increase the chemical resistance of the glasses according to the invention as well as their resistivity. The alkaline-earth metals 25 also have the effect of decreasing the melting temperature and the high-temperature viscosity of the glasses.

The advantages afforded by the glass compositions according to the invention will be more 30 fully appreciated from the examples given below.

A glass composition is made which contains the constituents below in the following proportions by weight:

35	SiO_2	69.60%
	Al_2O_3	0.90%
	ZrO_2	2.60%
	Na_2O	7.10%
	K_2O	2.90%
	CaO	10.50%

MgO	2.00%
SrO	3.90%
Fe ₂ O ₃	< 0.15%
Other oxides	< 0.50%.

5 The glass composition has the following properties:

↳ φ coefficient:	0.77 N/(mm ² . °C)
↳ Expansion coefficient α_{20-300} :	76.6 × 10 ⁻⁷ °C ⁻¹
↳ Modulus of elasticity:	78.6 × 10 ³ N/mm ²
10 ↳ Poisson's coefficient:	0.22
↳ φ ² .c/a	1.64 MPa ² /°C ²
↳ Softening point:	805 °C
↳ Liquidous temperature T_{liq} :	1160 °C
↳ Temperature $T_{log\eta=2}$,	
15 corresponds [sic] to a viscosity such that $log\eta = 2$:	1500 °C
↳ Temperature $T_{log\eta=3.5}$,	
corresponds [sic] to a viscosity such that $log\eta = 3.5$:	1176 °C
20 ↳ Temperature $T_{log\eta=4}$,	
corresponds [sic] to a viscosity such that $log\eta = 4$:	1100 °C

It is apparent first of all, from the liquidus temperature, from $T_{log\eta=2}$, which is the temperature in the 25 melting bath, and from $T_{log\eta=3.5}$, which is the chosen entry temperature of the glass on the bath of molten metal, that the glass composition may be melted in a melting furnace and that the forming process (float process) on a bath of tin poses no problem.

30 Sheets of glass were thus produced with thicknesses of between 5 and 10 mm. After having subjected their edges to a polishing treatment, the sheets of glass were toughened, in a horizontal position, in a conventional air toughening plant.

35 Next, the sheets of glass were fitted in frames with rabbet depths varying from 10 mm to 25 mm.

It has proved to be the case that the glazing panels thus produced according to the invention showed, in fire-withstand tests in accordance with the standard

DIN 4102 or the standard ISO/DIS 834-1, that they met the conditions of fire-resistance classes G 30 to G 120 depending on their thickness and on the depth of the frame's rabbet.

5 The glass composition described below, which may also be melted and obtained in the form of a ribbon using the float technique, may also be used for producing fireproof glazing meeting the conditions of the G fire-resistance classes:

10	SiO ₂	74.40%
	Al ₂ O ₃	0.95%
	Na ₂ O	9.05%
	K ₂ O	0.45%
	CaO	9.10%
15	MgO	5.65%
	Fe ₂ O ₃	0.10%
	Other oxides	0.30%.

It has the following properties:

20	↳ φ coefficient:	0.71 N/(mm ² .°C)
	↳ Expansion coefficient α ₂₀₋₃₀₀ :	75.6 × 10 ⁻⁷ °C ⁻¹
	↳ Modulus of elasticity:	75.4 × 10 ³ N/mm ²
	↳ Poisson's coefficient:	0.20
	↳ φ ² .c/a	1.56 MPa ² /°C ² .

CLAIMS

1. Glass composition of the silica-soda-lime type, intended for the manufacture of substrates or sheets,
5 **characterized in that** the glass composition has a ϕ coefficient of between 0.50 and 0.85 N/(mm².°C), a working point of less than 1200°C and in that it satisfies the relationship:

$$\phi^2 \cdot c/a < 2 \text{ MPa}^2/\text{°C}^2.$$

10 2. Glass composition according to Claim 1, **characterized in that** it satisfies the relationship:

$$0.70 \text{ MPa}^2/\text{°C}^2 < \phi^2 \cdot c/a.$$

3. Glass composition according to either of Claims 1 and 2, **characterized in that** it has a softening point 15 of greater than 750°C.

4. Glass composition according to one of Claims 1 to 3, **characterized in that** it has a strain point of greater than 570°C and preferably greater than 600°C.

5. Glass composition according to one of Claims 1 20 to 4, **characterized in that** the working point is less than 1190°C.

6. Glass composition according to one of Claims 1 to 5, **characterized in that** the thermal expansion coefficient α_{20-300} is between 60 and $85 \times 10^{-7}\text{°C}$.

25 7. Glass composition according to one of the preceding claims, **characterized in that** it contains the constituents below in the following proportions by weight:

	SiO ₂	55 - 75%
30	Al ₂ O ₃	0 - 7%
	ZrO ₂	0 - 8%
	Na ₂ O	5 - 10%
	K ₂ O	0 - 8%
	CaO	8 - 12%.

35 8. Glass composition according to Claim 7, **characterized in that** it satisfies, in proportions by weight:

$$12\% \leq \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20\%.$$

9. Glass composition according to either of Claims 7 and 8, **characterized in that** it contains the constituents below in the following proportions by weight:

5	SiO ₂	69.60%
	Al ₂ O ₃	0.90%
	ZrO ₂	2.60%
	Na ₂ O	7.10%
	K ₂ O	2.90%
10	CaO	10.50%
	MgO	2.00%
	SrO	3.90%
	Fe ₂ O ₃	< 0.15%
	Other oxides	< 0.50%.

15 10. Composition according to either of Claims 7 and 8, **characterized in that** it contains the constituents below in the following proportions by weight:

	SiO ₂	74.40%
	Al ₂ O ₃	0.95%
20	Na ₂ O	9.05%
	K ₂ O	0.45%
	CaO	9.10%
	MgO	5.65%
	Fe ₂ O ₃	0.10%
25	Other oxides	0.30%.

11. Glass composition according to one of the preceding claims, **characterized in that** it is capable of being converted into glass ribbon form using the float process of casting it into a bath of molten tin.

30 12. Use of the glass compositions as defined by any one of the preceding claims for the manufacture of monolithic glazing panels resistant to fire according to the G fire resistance classes.

13. Use of the glass compositions as defined by any 35 one of Claims 1 to 11 for the manufacture of substrates for emissive screens of the plasma-screen, electroluminescent-screen or cold-cathode-screen type, in particular using a sheet of glass cut from a ribbon

of glass obtained by floating the glass on a bath of molten metal.



UNITED STATES PATENT AND TRADEMARK OFFICE

I, Roger Walter GRAY MA, DPhil, CPhys,
translator to RWS Group plc, of Europa House, Marsham Way, Gerrards Cross,
Buckinghamshire, England declare;

1. That I am a citizen of the United Kingdom of Great Britain and Northern Ireland.
2. That I am well acquainted with the French and English languages.
3. That the attached is, to the best of my knowledge and belief, a true translation into the English language of the accompanying copy of the specification filed with the application for a patent in France on April 30, 1997 under the number 97/05,364 and the official certificate attached hereto.
4. That I believe that all statements made herein of my own knowledge are true and that all statements made on information and belief are true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the patent application in the United States of America or any patent issuing thereon.

A handwritten signature in black ink, appearing to read "Roger W. Gray".

For and on behalf of RWS Group plc
The 20th day of April 2001



P A T E N T

UTILITY CERTIFICATE - CERTIFICATE OF ADDITION

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The Director-General of the Institut National de la Propriété Industrielle certifies that the attached document is a true copy of an application for industrial property titleright filed at the Institute.

Drawn up in Paris, 10 MARCH 1998

On behalf of the Director-General of the
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The Patent Department Head

(signature)

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PATENT, UTILITY CERTIFICATE

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DATE OF SUBMISSION OF THE DOCUMENTS		30 APR. 1997			
NATIONAL REGISTRATION		97/05,364			
DEPARTMENT OF FILING		75			
DATE OF FILING		30 APR 97			
2. APPLICATION		Nature of the industrial property right <input checked="" type="checkbox"/> patent <input type="checkbox"/> divisional application \rightarrow initial application \downarrow <input type="checkbox"/> utility certificate <input type="checkbox"/> conversion of a European patent application <input checked="" type="checkbox"/> patent <input type="checkbox"/> utility certificate No. The applicant, as a physical person, asks to pay the fee by instalments <input type="checkbox"/> yes <input checked="" type="checkbox"/> no			
Compilation of the search report		<input checked="" type="checkbox"/> deferred	<input type="checkbox"/> immediate		
Title of the invention (maximum 200 characters)		SILICA-SODA-LIME GLASS COMPOSITIONS AND THEIR APPLICATIONS			
3. APPLICANT(S)		SIREN No.	APE-NAF code		
		Name and forenames (underline the surname) or company name			Legal form
		SAINT-GOBAIN VITRAGE			Société Anonyme
Nationality/Nationalities		FRENCH			
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18, avenue d'Alsace F-92400 COURBEVOIE					FRANCE
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4. INVENTOR(S)		The inventors are the applicants	<input type="checkbox"/> yes	<input checked="" type="checkbox"/> no	If the answer is no, provide a separate designation
5. REDUCTION OF THE RATE OF FEES		<input type="checkbox"/> requested for the first time	<input type="checkbox"/> requested prior to filing; attach copy of the favourable decision		
6. PRIORITY DECLARATION OR APPLICATION FOR THE BENEFIT OF THE FILING DATE OF A PRIOR APPLICATION					
Country of origin		Number	Filing date	Nature of the application	
7. DIVISIONS previous to the present application		No.	date	No.	date
1. SIGNATURE OF THE APPLICANT OR REPRESENTATIVE (name and capacity of the signatory - registration No.)		SIGNATURE OF THE RECEIVING OFFICIAL		SIGNATURE AFTER REGISTRATION OF THE APPLICATION AT THE INPI	
[Rubber stamp of SAINT-GOBAIN RECHERCHE]		(illegible signature)			
(signature) Stéphane LE CAM					

DOCUMENT CONTAINING CORRECTIONS

(FRENCH) PAGE(S) OF THE DESCRIPTION OR OF THE CLAIMS OR SHEET(S) OF DRAWINGS			R.M.*	DATE OF THE CORRESPONDENCE	DATE STAMP OF THE CORRECTOR
Amended	Omitted	Added			
10.11			X	29.7.97	11 AUGUST 1997 T L

* A change made in the wording of the original claims, unless the change derives from the provisions of Article 28 of the decree of 19th September 1979, is indicated by the reference "R.M." (amended claims).

SILICA-SODA-LIME GLASS COMPOSITIONS AND THEIR APPLICATIONS

The subject of the present invention is glass
5 compositions suitable for being converted into a ribbon
of glass from which may be cut sheets which have good
heat resistance. These sheets may more particularly be
used for producing fireproof glazing panels or for
serving as substrates for the manufacture of plasma
10 screens, electroluminescent screens and cold-cathode
screens (field-emission display).

The glass used at the start for producing such
substrates is a glass belonging to the family of
silica-soda-lime glasses normally used for
15 manufacturing glazing panels intended for buildings or
motor vehicles. Although this type of glass is
generally satisfactory with regard to its chemical
resistance and its flatness, its temperature withstand
occasionally leaves something to be desired.

20 During manufacture of emissive screens of the
plasma-screen type, the substrate is subjected to
several heat treatments for the purpose of stabilizing
the dimensions of the said substrate and of fixing a
series of layers of various compounds, such as enamels,
25 deposited on its surface. Fixing these relatively thick
layers requires the substrate to be heated to
temperatures greater than 550°C. If the expansion
coefficient of the silica-soda-lime glass used is of
the same order of magnitude as that of the compounds
30 deposited on its surface, its temperature withstand is
insufficient and it is necessary to place it on a
ground slab during the heat treatments in order to
avoid any deformation.

The glasses used for the manufacture of
35 fireproof glazing panels generally belong to the family
of borosilicate glasses. These glasses, which have very
good heat resistance and heat-shock resistance, are
generally characterized by a low expansion coefficient.
The latter property does not allow high stresses to be

developed in these glasses by thermal toughening, and the increase in their mechanical strength obtained by this means proves to be limited.

Novel families of glass compositions have been
5 developed and described in the patent WO-96/11887 so as to mitigate these drawbacks, especially so as to be able to manufacture sheets or substrates undergoing virtually zero deformation during heat treatments of the order of 550 to 600°C and capable of generating, by
10 thermal toughening, stress levels comparable to those obtained with standard silica-soda-lime glass.

However, it appears that these glasses may undergo breaks during the deposition of certain layers, including when the methods of depositing these layers
15 result in local temperatures of the glass which do not exceed about a hundred degrees Celsius.

The inventors have thus sought to remedy these breaks, which, albeit infrequent, disrupt the manufacturing plants.

20 The subject of the invention is novel glass compositions allowing the manufacture of substrates whose deformation remains virtually zero when they are subjected to temperatures of about 600°C and which do not deteriorate when depositing layers on their
25 surface, i.e. which do not break immediately and which do not have flaws which may lead to an eventual break.

This objective is achieved according to the invention by a glass composition intended for the manufacture of thermally stable substrates or sheets,
30 the said glass composition having a ϕ coefficient of less than 0.84 N/(mm².°C), its strain-point temperature being greater than 507°C and its electrical resistivity being such that $\log \rho_{(250^{\circ}\text{C})}$ is greater than 6.6. The ϕ coefficient is defined according to the relationship:

$$35 \quad \phi = \alpha \cdot E / (1 - \mu)$$

where α : expansion coefficient

E : modulus of elasticity

μ : Poisson's ratio.

It is commonly accepted that glass no longer behaves in a viscous manner below a characteristic temperature called the strain-point temperature which corresponds to a viscosity of the order of $10^{14.5}$ poise.

5 This temperature is therefore a useful reference point for evaluating the temperature withstand of a glass.

It has proved to be the case in tests that, in particular, the combination of these values of strain-point temperatures [sic] and of the ϕ coefficient allow

10 the production of a substrate or sheet which is thermally stable and undergoes no deterioration or break during the layer-deposition treatment phases. The electrical resistivity values limit, in particular, the diffusion into the glass of, for example, silver ions

15 contained in the layers deposited on the surface of the substrate.

According to a preferred embodiment of the invention, the expansion coefficient of the glass composition, measured in a known manner by differences

20 in expansion at temperatures of 25°C and 300°C, is between 65 and $88 \times 10^{-7}^{\circ}\text{C}^{-1}$. Such values are particularly advantageous for their compatibility with those of the glass frits normally used for producing, for example, barriers for plasma screens.

25 Also preferably, the expansion coefficient is between 80 and $85 \times 10^{-7}^{\circ}\text{C}^{-1}$.

A more particularly advantageous glass composition according to the invention, in particular in terms of thermal-break resistance and cost, has a ϕ

30 coefficient of less than $0.8 \text{ N}/(\text{mm}^2 \cdot ^\circ\text{C})$ and preferably greater than $0.7 \text{ N}/(\text{mm}^2 \cdot ^\circ\text{C})$.

Also to decrease the cost of the glass composition, the latter advantageously has a strain-point temperature of less than 590°C and preferably

35 less than 580°C.

Also advantageously, and in particular for decreasing the compaction of the substrate during treatment at relatively high temperatures, the glass composition has a strain-point temperature of greater

than 530°C and preferably greater than 550°C. Such strain-point temperature values allow good control and high precision in the deposition operations which may be carried out at temperatures of about 600°C.

5 Also preferably, the electrical resistivity of the glass composition according to the invention is such that $\log \rho_{(250^{\circ}\text{C})}$ is greater than 8; this makes it even more possible to prevent diffusion into the glass of ions originating from the deposited layers.

10 According to a preferred embodiment of the invention, the glass composition contains the constituents below in the following proportions by weight:

	SiO ₂	55 - 75%
15	Al ₂ O ₃	0 - 5%
	ZrO ₂	3 - 8%
	Na ₂ O	4.5 - 8%
	K ₂ O	3.5 - 7.5%
	CaO	7 - 11%.

20 The glass compositions according to the invention have, in particular, the advantage of being able to be melted and converted into glass ribbon form at temperatures close to those adopted for the manufacture of conventional silica-soda-lime glass.

25 In this regard, SiO₂ plays an essential role. In the context of the invention, the SiO₂ content must not exceed approximately 75%; above this, the melting of the batch and the refining of the glass require high temperatures which cause accelerated wear of the
30 furnace refractories. Below 55% by weight of SiO₂, the glasses according to the invention are insufficiently stable.

35 Alumina acts as a stabilizer. This oxide to some extent increases the chemical resistance of the glass and increases the strain-point temperature. The percentage of Al₂O₃ must not exceed 5% and preferably 3%, in particular so as not to increase unacceptably the viscosity of the glass at high temperatures.

ZrO₂ also acts as a stabilizer. This oxide to a certain extent increases the chemical resistance of the glass and increases the strain-point temperature. The percentage of ZrO₂ must not exceed 8% for fear of making
5 the melting operation too difficult. Although this oxide is difficult to melt, it has the advantage of not increasing the viscosity of the glasses according to the invention at high temperatures, in the same way as SiO₂, and Al₂O₃. The oxide B₂O₃, may also be present with a
10 content of at most 3%, and preferably less than 2%. This oxide makes it possible to increase the fluidity of the glass without lowering the strain point.

Overall, the melting of the glasses according to the invention remains within acceptable temperature
15 limits, as long as the sum of the SiO₂, Al₂O₃, and ZrO₂ oxide contents remains less than or equal to 75%. The expression "acceptable limits" should be understood to mean that the temperature of the glass corresponding to log η = 2 does not exceed approximately 1550°C and
20 preferably 1510°C.

Moreover, it seems that these glasses lead to little corrosion of the refractories of the AZS (alumina-zirconia-silica) type normally used in this type of furnace. These glasses thus guarantee that the
25 operating time of the furnace is optimized.

Moreover, there is a sufficient difference in the glass compositions according to the invention between the glass-forming temperature and its liquidus temperature; this is because, in the float-glass
30 technique in particular, it is important that the liquidus temperature of the glass remain equal to or less than the temperature corresponding to log η = 3.5, which is the case with the glasses according to the invention. This difference is advantageously at least
35 10°C to 30°C. These differences or working ranges, which might seem "narrow" for standard silica-soda-lime glasses intended for manufacturing glazing panels, are sufficient here to ensure high-quality forming without adopting excessively extreme conditions for operating

the furnace. This is because the glasses are quite special, for applications of the high-tech, high value-added type, such as plasma screens, in which one may "indulge" in very precise control and suitability of
5 the operation of the furnace: "accessible" working ranges are maintained without upsetting the furnace or exposing it to risk.

The influence of the other oxides on the ability of the glasses according to the invention to be
10 melted and floated on a metal bath, as well as their properties, is as follows: the oxides Na_2O and K_2O make it possible to maintain the melting temperature of the glasses according to the invention and their high-temperature viscosities within the limits indicated
15 above. To do this, the sum of the contents of these oxides remains greater than 8% and preferably greater than 10%. Compared with an ordinary silica-soda-lime glass, the simultaneous presence of these two oxides in the glasses according to the invention, sometimes in
20 similar proportions, considerably increases their chemical resistance, more specifically their hydrolytic resistance, as well as their electrical resistivity. Increasing the electrical resistivity of the glasses decreases the diffusion of ions, for example silver
25 ions, coming from the layers deposited on the surface of the substrates, into the glass, especially in the case of the production of plasma screens. Increasing the electrical resistivity of the glasses is also advantageous in certain applications, more specifically
30 when they are used as a substrate for cold-cathode screens. In these screens, surface electric fields are created which cause a localized concentration of electrons. This concentration may cause, in reaction, undesirable migration of the alkali elements if the
35 resistivity of the glass is not high enough, as in the case of an ordinary silica-soda-lime glass.

However, although both types of alkali metal oxides Na_2O and K_2O are necessary, it is preferable, if it is desired to increase their overall content, to

favour an increase in the K₂O content, which has the advantage of increasing the fluidity of the glass without lowering the strain point, and hence without excessively compromising the hardness properties of the
5 glass after forming. In addition, K₂O is conducive to decreasing the modulus of elasticity in the glass compositions according to the invention. Preferably, a K₂O/Na₂O weight percentage ratio of at least 1.2, and preferably at least 1.4, is thus advantageously
10 provided.

Provision may also be made to incorporate lithium oxide Li₂O in the glass composition according to the invention, especially as a fluxing agent, with contents of possibly as much as 3% and preferably not
15 exceeding 1%.

The alkaline-earth metal oxides introduced into the glasses according to the invention have the overall effect of raising the strain-point temperature, and it is for this reason that the sum of their weight
20 contents must be at least equal to 12%. Above approximately 20%, the ability of the glasses to devitrify may increase to an extent incompatible with the process of floating on a metal bath. In order to keep the devitrification of the glasses within
25 acceptable limits, their CaO and MgO weight contents must not exceed 11% and 5% respectively. The MgO content is preferably equal to or less than 2%.

MgO, CaO and, to a lesser degree, SrO make it possible to increase the strain-point temperature; BaO
30 and SrO make it possible to increase the chemical resistance of the glasses according to the invention as well as their resistivity. The alkaline-earth metals also have the effect of decreasing the melting temperature and the high-temperature viscosity of the
35 glasses.

However, BaO is preferably present with a content of less than 2%; these low contents make it possible to limit the formation of barium sulphate BaSO₄ crystals, which would impair the optical quality.

Although complete absence of BaO is not excluded, a low content is preferred because of the abovementioned properties of BaO. When BaO is present, it is possible as well to modify the substrate heat-treatment 5 conditions slightly in order to make them less conducive to the formation of BaSO_4 crystals.

The advantages afforded by the glass compositions according to the invention will be more fully appreciated from the examples combined in the 10 table attached as an annex.

This table gives, for each of these examples, the chemical formulations with the contents expressed in percentages by weight, the values of the ϕ coefficient expressed in $\text{N}/(\text{mm}^2 \cdot ^\circ\text{C})$, the strain-point 15 temperature values of the glasses T_{sp} , the thermal expansion coefficients $\alpha(25-300^\circ\text{C})$ of the glasses in $^\circ\text{C}^{-1}$, the log of their resistivities in ohm.cm $\log \rho$, their liquidus temperatures T_{liq} , their temperatures at viscosities, in poise, corresponding respectively to 20 $\log \eta = 2$ and $\log \eta = 3.5$, $T_{\log \eta=2}$ and $T_{\log \eta=3.5}$. All temperatures are expressed in degrees Celsius.

From the tests carried out and/or given in the annex, and more particularly from the last three lines, when the measurements were made, which indicate 25 temperatures corresponding, in respect of the first, to the viscosity $T_{\log \eta=2}$, which is the temperature in the melting bath, in respect of the second, to the viscosity $T_{\log \eta=3.5}$, which is the chosen entry temperature of the glass on the bath of molten metal, and finally, 30 in respect of the third, to the liquidity, it is firstly verified that the glasses according to the invention may be melted in a melting furnace and that their forming on a bath of tin poses no problem.

It was thus possible to obtain glasses 35 according to the invention, using the float technique in the form of a ribbon having a controlled thickness, which may vary from 0.5 to 10 mm. Sheets of glass were then cut to the desired format and subjected to a heat treatment whose purpose was to stabilize the dimensions

of the said sheets. Next, layers were deposited on these sheets, such as those leading to the production of plasma screens.

First of all, the substrates exhibited quite 5 satisfactory thermal stability. Moreover, during the layer-deposition treatments, no break of the said substrates occurred.

The glass compositions thus presented according to the invention therefore meet the stipulated 10 requirements, that is to say that they make it possible to produce substrates or plates which are thermally stable and have an increased thermal-break resistance over the glasses already known.

Composition	1	2	3	4	5	6	7	8	9	10	11	12
SiO ₂	68	65	64.5	65	67.5	64.5	66	65	69	67.5	69.5	70
Al ₂ O ₃	0	0	1	1	1	0	1	0	0	0	1	0.5
ZrO ₂	4	7.5	7	6	3	6.5	6.5	6.5	4	4.5	3	3
Na ₂ O	5	5	5	5.5	5	7.5	7	9	6	5	6.5	6.5
K ₂ O	7.5	7.5	7.5	7.5	7	5.5	4.5	4	4	6	3.5	3.5
CaO	11	11	11	10.5	10.5	10	11	9.5	11	11	11	11
MgO	0.5	0	0	0	1.5	2	2	2	2	2	2	1.5
BaO	0	0	0	0	1.5	0	0	0	0	0	0	0
SrO	4	4	4	3.5	4	3	3	3	4	3.5	3.5	4
φ	0.75	0.79	0.79	0.79	0.75	0.79	0.8	0.8	0.74	0.76	0.75	0.73
T _{s.p.}	580	583	581	582	573	567	570	558	-	-	-	-
log p _(250°C)	-	-	-	-	-	7.9	-	-	-	-	-	-
α	82	81	81	81	81	79.8	80.1	83.2	78.1	77.4	73.1	75.5
T _{logn=2}	1496	1491	1497	1491	1498	1500	1490	1480	1490	1485	1500	1498
T _{logn=3.5}	1171	1186	1189	1186	1171	1185	1175	1170	1170	1173	1180	1169
T _{liq}	-	-	-	-	-	1120	1140	1090	-	-	-	-

"-" : value not measured

CLAIMS

1. Glass composition intended for the manufacture of a thermally stable substrate or sheet, **characterized in that** it has a φ coefficient of less than 0.84, **in that** its strain point is greater than 507°C **and in that** its electrical resistivity is such that $\log \rho_{(250^\circ\text{C})}$ is greater than 6.6.
2. Glass composition according to Claim 1, **characterized in that** its expansion coefficient is between 65 and $88 \times 10^{-7}^\circ\text{C}^{-1}$ and preferably between 80 and $85 \times 10^{-7}^\circ\text{C}^{-1}$.
3. Glass composition according to either of Claims 1 and 2, **characterized in that** the φ coefficient is less than 0.8 and preferably greater than 0.75.
4. Glass composition according to one of the preceding claims, **characterized in that** its strain-point temperature is between 530 and 590°C and preferably between 550 and 580°C.
5. Glass composition according to one of the preceding claims, **characterized in that** its electrical resistivity is such that $\log \rho(250^\circ\text{C})$ is greater than 8.
6. Glass composition according to one of the preceding claims, **characterized in that** it contains the constituents below in the following proportions by weight:

SiO ₂	55 - 75%
Al ₂ O ₃	0 - 5%
ZrO ₂	3 - 8%
Na ₂ O	4.5 - 8%
K ₂ O	3.5 - 7.5%
CaO	7 - 11%.
7. Glass composition according to Claim 6, **characterized in that** it satisfies in weight percent the following:
 $K_2O/Na_2O \geq 1.2$ and preferably $K_2O/Na_2O \geq 1.4$.

8. Glass composition according to either of Claims 6 and 7, **characterized in that** it satisfies, in proportions by weight:

$$12\% \leq \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20\%.$$

5 9. Glass composition according to one of Claims 6 to 8, **characterized in that** the weight content of BaO is less than 2%.

10. Glass composition according to one of the preceding claims, **characterized in that** it is capable 10 of being converted into glass ribbon form using the float process of casting it into a bath of molten tin.

11. Use of the glass compositions as defined by any one of the preceding claims for the manufacture of substrates for emissive screens of the plasma-screen, 15 electroluminescent-screen or cold-cathode-screen type, in particular using a sheet of glass cut from a ribbon of glass obtained by floating the glass on a bath of molten metal.

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	CaO	7 - 11%.

7. Glass composition according to Claim 6, **characterized in that** it satisfies in weight percent the following:

$$K_2O/Na_2O \geq 1.2 \text{ and preferably } K_2O/Na_{20}O \geq 1.4.$$

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$$12\% \leq \text{MgO} + \text{CaO} + \text{SrO} + \text{BaO} \leq 20\%.$$

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